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**IN SITU SURFACE X-RAY CRYSTALLOGRAPHY OF  
ELECTROCHEMICALLY DEPOSITED BI ON AG(111):  
STRUCTURE, COMPRESSIBILITY, AND ANISOTROPY**

by

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## ABSTRACT

We have performed in-situ x-ray diffraction measurements on an underpotentially deposited monolayer of Bi on Ag(111). The Bi forms a two-dimensional nearly centered rectangular structure that is uniaxially commensurate with the Ag(111) surface. The Bi monolayer compresses uniaxially along the incommensurate direction. Neither the Bi structure nor its compressibility is affected by the presence or absence of chloride in the electrolyte. Initial crystallographic analysis reveals that the nearly centered atom is displaced by approximately  $0.35\text{\AA}$  along the commensurate direction, and that the atomic disorder in the monolayer is anisotropic.

## I. Introduction

The electrodeposition of metals can occur in two distinct steps. First, a monolayer or sometimes a monolayer and bilayer can be deposited at a potential positive of the Nernst potential for bulk deposition. This is termed underpotential deposition (UPD) (1). Then at the Nernst potential, bulk deposition occurs. The fundamental question that all our studies address is: What roles do the adsorbate-adsorbate, adsorbate-substrate, and electrolyte-adsorbate interactions play in determining the structure and the properties of UPD layers? By systematically determining the structures and properties of different UPD systems we hope to gain insight into the formation and growth of UPD layers and bulk electrodeposition.

Recently, rapid progress has been made in determining the in situ structure of UPD deposited layers due to the advent of direct in situ structural techniques. There are many techniques (e.g., STM, EXAFS, and X-ray Standing Waves) that probe the local

order of the liquid-solid interface in situ (2-4). Grazing incidence X-ray scattering (GIXS), on the other hand, directly probes the long-range order and has recently been used to determine the atomic structure of UPD adlayers (5-9).

In this paper, we discuss recent progress in our UPD adlayer research program. Previously we determined the structures of UPD Pb and UPD Tl on Ag(111) (5-8). Both of these systems form incommensurate hexagonal close-packed structures on Ag(111). This paper discusses our newest results for UPD Bi on Ag(111) (9). We have found that Bi/Ag(111) is very different from that of Tl and Pb: Bi forms a uniaxially commensurate rectangular lattice instead of an incommensurate hexagonal adlayer. There are two Bi atoms per rectangular unit cell, with the Bi atom near the center of the cell offset along the commensurate direction. Our initial crystallographic analysis shows that the Bi monolayer also has anisotropic disorder: the atomic disorder in the incommensurate direction is larger than in the commensurate direction. By varying the applied potential, the monolayer compresses uniaxially. Although the presence of chloride dramatically affects the shape of the adsorption and desorption peaks in the Bi cyclic-voltammogram, we find no structural differences in the Bi monolayer for chloride containing and chloride "free" electrolytes. For this system, both the adsorbate-substrate interaction and a fortuitous match between the Bi and Ag produce a Bi layer commensurate with the Ag substrate in one direction: this is very different than UPD Tl and Pb layers where the substrate potential only produces a weak modulation of these incommensurate layers.

## II. Experimental Aspects

The complete experimental details are described elsewhere (9). Here we summarize only the most important aspects. Our experiments were all performed in situ, under potential control and at room temperature. The electrochemical cell is the same as that used in our earlier studies (5-8). The electrolytes were prepared from Aldrich ultrapure reagents and "nanopure" (Barnstead) deionized water. The Ag substrates were epitaxially grown by vapor deposition onto freshly cleaved mica. This process produces Ag films with large flat defect free (111) faces. The Bi monolayer was electrochemically deposited with the cell inflated so that there was a relatively thick layer of electrolyte

covering the Ag film. This minimized the electrochemical cell resistance and allowed high quality electrochemical characterization of the Bi/Ag(111) system during the diffraction experiments. After depositing the Bi monolayer the electrolyte was partially removed to minimize the scattering from the electrolyte and the surface diffraction data was measured through the thin layer of electrolyte remaining above the electrode.

Since the shape of the adsorption and desorption peaks in the cyclic-voltammogram of Bi are sensitive to the presence of chloride, see figure 1, we investigated the structure and compressibility of the Bi monolayer with two different electrolytes (9). Both a chloride containing solution of 0.1M  $\text{HClO}_4$  with 0.35 mM NaCl and 2.5 mM  $\text{Bi}_2\text{O}_3$ , and a chloride "free" solution of 0.1M  $\text{HClO}_4$  with 2.5 mM  $\text{Bi}_2\text{O}_3$  were used. All potentials were measured relative to the Ag/AgCl (3 M KCl) reference electrode in the diffraction cell. For the experiments in the chloride containing electrolyte, the Ag/AgCl reference electrode was isolated from the cell by a single porous frit, but to prevent contamination during the experiments in the chloride "free" electrolyte, a double junction reference electrode was used; the reference electrode was isolated behind a second porous junction filled with 0.1 M  $\text{HClO}_4$ .

The X-ray data was collected at the NSLS beam line X20C (10). An incident energy of 10005 eV was selected with a Si(111) double monochromator. The sample was aligned by using the bulk Ag reflections and the data was collected in the symmetric ( $\omega=0$ ) mode (11).

### III. Experimental Results

The in-plane surface X-ray scattering pattern for Bi on Ag is shown in figure 2. Because the Ag(111) surface is 3-fold symmetric, the complete scattering pattern consists of a superposition of 3 identical patterns rotated 120 degrees from each other. The complete pattern is shown in figure 2(a). For simplicity, figure 2(b) only shows one of the three domains.

The surface diffraction from the Ag and Bi are indicated in figure 2(b) by the open

and filled circles, respectively. The filled circle sizes denote the approximate relative intensity of each Bi peak. The Bi(20) peak coincides with the  $\text{Ag}1/3[4\bar{2}\bar{2}]$  surface rod indicating that the Bi monolayer is commensurate with the Ag in this direction. Two peaks that would appear in a simple centered rectangular pattern were not observed. The Bi(01) peak could not be measured due to the presence of an intense mica substrate peak at the same position. The Bi(03) peak was not detected indicating that the rectangular lattice has a basis that destructively interferes at this position.

Our proposed structure is shown in figure 3. From the rectangular scattering pattern we conclude the Bi structure is also rectangular. The absence of the Bi(03) means that there is a centered Bi atom half way between the rectangular Bi atoms in the Bi[01] direction. However, the presence of the Bi(30), Bi(10), and Bi(21) peaks proves this 'centered' Bi atom is not centered in the Bi[10] direction. Taken together, the observed scattering indicates a rectangular Bi lattice with two atoms per rectangular unit cell that is commensurate with the Ag(111) surface in the  $\text{Ag}[\bar{2}11]$  direction but incommensurate with the Ag in the  $\text{Ag}[01\bar{1}]$  direction. Furthermore, the peak positions of the X-ray scattering were independent of the presence of chloride showing that the chloride does not affect the structure of the Bi lattice.

We also measured the intensities of the Bi Bragg rods and of the Ag surface rod in detail. The Bi scattering intensities contain detailed information on the location of the Bi atoms in the unit cell while the Ag surface rod scattering contains information on the epitaxy between the Bi monolayer and the Ag(111) surface. Our initial crystallographic analysis reveals that the nearly centered atom is displaced by approximately  $0.35 \text{ \AA}$  along the commensurate direction. This displacement shortens two of the Bi-Bi bond distances while lengthening two others, perhaps reflecting the tendency towards covalent bonding in Bi. An anisotropic Debye-Waller factor is required to fit the data indicating more atomic disorder in the incommensurate direction than in the commensurate direction. Our preliminary analysis shows that the Bi atoms have rms displacements of  $0.2 \text{ \AA}$  and  $0.3 \text{ \AA}$  in the commensurate and incommensurate directions, respectively. This implies that the commensurate Bi atoms have larger adsorbate-substrate interactions than the incommensurate Bi atoms, thus, keeping the commensurate atoms closer to their equilibrium positions. Our analysis of the Ag rod intensities places the commensurate Bi

atoms in between the  $\text{Ag}[01\bar{1}]$  rows. As figure 3 shows, the Bi atoms lie in between the Ag surface atoms (i.e., in the valleys).

Measurements on Pb and Tl on  $\text{Ag}(111)$  revealed that these UPD monolayers both compress isotropically (5,7,8). This is very different than Bi which compresses uniaxially. In figure 4, the Bi rectangular lattice constants  $a$  and  $b$  are plotted versus the applied potential. The open circles indicate data taken with chloride in the electrochemical cell and the filled circles indicate the chloride "free" data. The position of the Bi atoms that are commensurate with the Ag surface atoms in the  $\text{Ag}[\bar{2}11]$  direction remain fixed with,  $a_{\text{Bi}} = a_{\text{Ag}}\sqrt{3} = 5.005\text{\AA}$ , while the positions of the Bi atoms along the incommensurate,  $\text{Ag}[01\bar{1}]$  direction, compress as the potential is lowered,  $b_{\text{Bi}} = 4.484\text{--}4.566\text{\AA}$ . Our data clearly show that the presence of chloride does not influence the compression of the Bi monolayer. From the slope of the compression in Figure 4(b), the two-dimensional isothermal compressibility ( $\kappa_{2D}$ ) can be determined (9). We find that  $\kappa_{2D} = 0.79 \pm 0.04 \text{ \AA}^2/\text{eV}$  for  $\text{Bi}/\text{Ag}(111)$ . The Bi compressibility is somewhat lower than the compressibility for Tl ( $\kappa_{2D} = 1.6\text{--}2.0 \text{ \AA}^2/\text{eV}$ ) and Pb ( $\kappa_{2D} = 1.2\text{--}1.6 \text{ \AA}^2/\text{eV}$ ). A simple 2-D free electron gas model underestimates the Bi compressibility ( $\kappa_{2D} = 0.2 \text{ \AA}^2/\text{eV}$ ) but yields a compressibility of the right order of magnitude.

#### IV. Discussion

The Bi monolayer structure is determined by an interplay between the adsorbate-adsorbate and adsorbate-substrate interactions. Unlike UPD Pb and UPD Tl, both of which form incommensurate hexagonal close-packed structures on the  $\text{Ag}(111)$  surface, Bi forms a rectangular lattice on a hexagonal substrate. This is probably due to the close match between the  $\text{Ag}(111)$  surface atomic spacing and the spacing of the bulk hexagonal Bi (102) plane. But, even though the primary force determining the monolayer structure is the adsorbate-adsorbate interaction, the adsorbate-substrate interaction keeps the  $\text{Bi}[10]$  rows commensurate with the Ag substrate while the  $\text{Bi}[01]$  rows compress uniaxially. Therefore, in this system, the adsorbate-substrate interactions also plays an important role



in determining the monolayer structure.

The electrolyte-adsorbate interactions, on the other hand, do not influence the observed structure and consequently are not important in this system. UPD Bi on Ag(111) has been studied *ex situ* with LEED by Laguren-Davidson et al. (12). Although a detailed discussion can not be presented here, we have shown that their *ex situ* data supports our proposed *in situ* structure (9). This demonstrates that the monolayer structure, in this case, is independent from the detailed electrolyte-adsorbate interactions since both the *in situ* and *ex situ* structures are identical.

## V. Conclusions

Grazing incidence X-ray scattering has been used to determine the *in situ* structure of UPD Bi on Ag(111). From the Bi scattering we have concluded that Bi forms a uniaxially commensurate rectangular lattice with one of the two Bi atoms per unit cell near the center. The Bi scattering intensities show that the nominally "centered" atom is actually displaced along the commensurate direction by  $0.35\text{\AA}$ . An anisotropic Debye-Waller factor is required to fit the measured Bi intensities, revealing that the Bi atoms have more disorder along the incommensurate direction than along the commensurate direction. The Ag surface rod intensities have also been used to deduce the Bi-Ag epitaxy: the Bi atoms are adsorbed on the Ag surface in between the Ag[01 $\bar{1}$ ] rows. As the electrode potential is varied, the Bi monolayer compresses uniaxially. This allows the determination of the 2-D compressibility for Bi/Ag(111),  $\kappa_{2D} = 0.79 \pm 0.04 \text{ \AA}^2/\text{eV}$ .

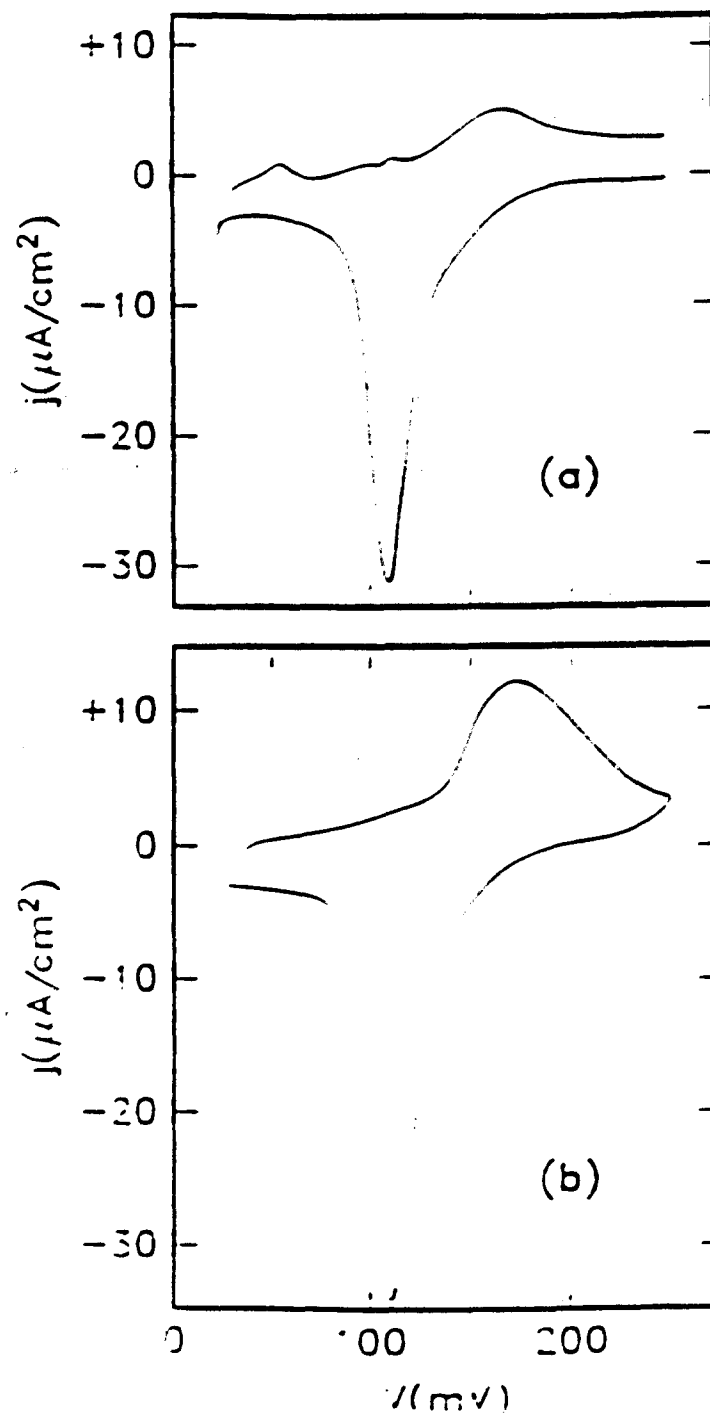
By determining the structure of Bi/Ag(111), we have gained insight into the relative contributions of the different forces that govern the monolayer structure. Hopefully this will further our understanding of the underlying mechanisms that determine the structural properties of electrochemically deposited layers.

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We thank Jean Jordan-Sweet and Brian Stephenson for their assistance with beam line X20C. This work was partially supported by the Office of Naval Research. It was performed at the National Synchrotron Light Source (NSLS), which is supported by the U.S. Department of Energy, Division of Material Sciences and Division of Chemical Sciences (DOE Contract No. DE-ACO2-76-CH00016).

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**Figure 1.** Cyclic voltammogram for the UPD of Bi on Ag(111) measured at a 2 mV/S sweep rate in two different electrolytes: (a) A chloride "free" solution (0.1 M  $\text{HClO}_4$  with 2.5 mM  $\text{Bi}_2\text{O}_3$ ); (b) a chloride containing solution (0.1 M  $\text{HClO}_4$  with 2.5 mM  $\text{Bi}_2\text{O}_3$  and 0.35 mM NaCl). The adsorption and desorption peaks are significantly larger and sharper in the chloride containing electrolyte.

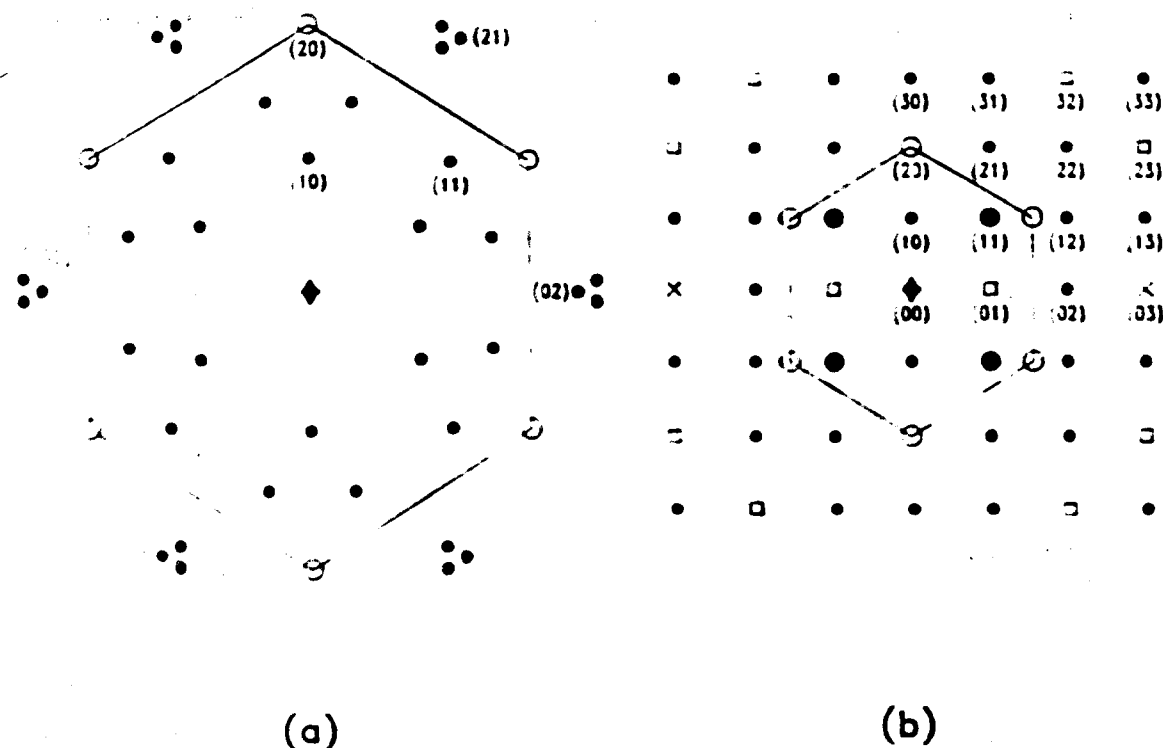


Figure 2. The surface X-ray diffraction pattern for Bi on Ag(111). (a) The measured diffraction pattern consisting of the superposition of incoherent scattering from three domains. (b) The X-ray pattern that would be observed from one domain. The open circles denote the Ag surface peaks: The filled circles represent the Bi monolayer peaks. Two peaks were not observed: The peaks at the open square positions were obscured by mica substrates peaks: the peaks at the cross positions were too weak to be measured.

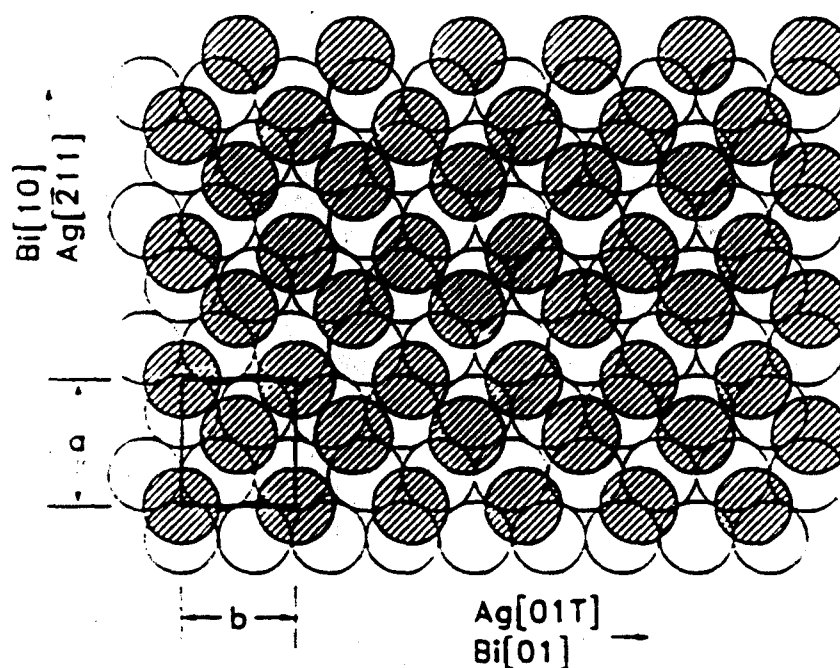
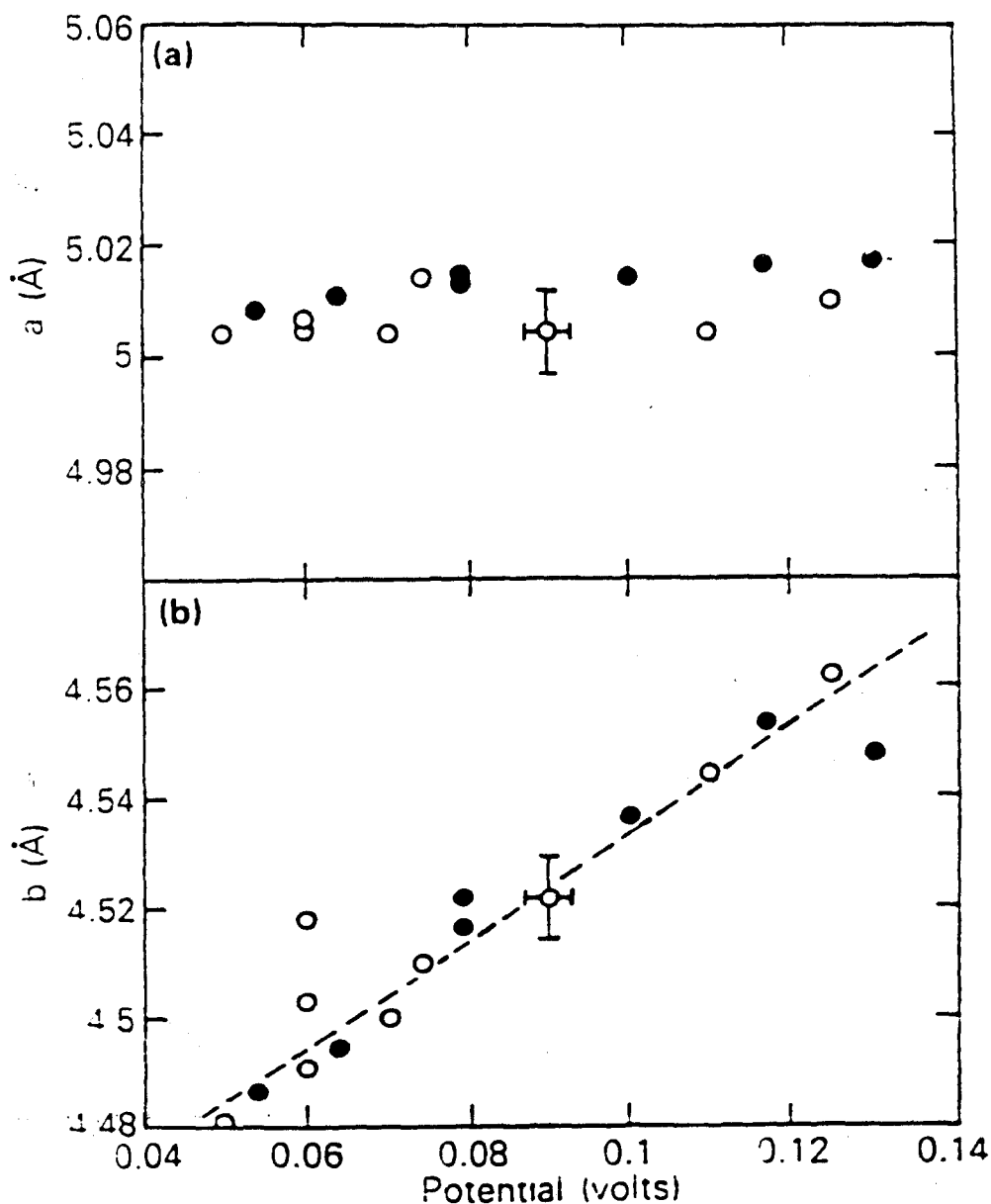


Figure 3. Structure of UPD Bi/Ag(111). The open circles represent the surface atoms of the Ag substrate and the shaded circles represent the Bi adatoms. The relative sizes of these circles correspond to the near neighbor spacing of bulk Ag ( $2.89\text{\AA}$ ) and bulk Bi ( $3.07\text{\AA}$ ). The Bi monolayer is commensurate in the  $a$  direction, ( $a_{\text{Bi}} = a_{\text{Ag}}\sqrt{3} = 5.005\text{\AA}$ ), but is incommensurate in the  $b$  direction, ( $b_{\text{Bi}} = 4.484\text{--}4.566\text{\AA}$ ).



**Figure 4.** Bi monolayer lattice constants versus electrode potential. The open and filled circles denote chloride containing and chloride "free" electrolytes, respectively. (a) The lattice constant  $a$  remains commensurate with the Ag surface. The average value is  $a = 5.007 \pm 0.002$  Å. (b) The lattice constant  $b$  compresses as the potential is lowered. The dashed line is a linear least square fit to the data with a slope  $db/dV = -0.95 \pm 0.05$  Å/V.